[DESCRIPTION]

FIELD OF THE INVENTION

The present invention relates to a negative-working heat-sensitive material which is suitable for making a lithographic printing plate by direct-to-plate recording and to a method for imaging said heat-mode recording material by means of an infrared laser.

BACKGROUND OF THE INVENTION

Lithographic printing is the process of printing from specially prepared surfaces, which contain a lithographic image consisting of areas that are capable of accepting ink (oleophilic areas) and areas that do not accept ink but are water-accepting (hydrophilic areas). In so-called wet lithographic printing methods, both water or an aqueous dampening liquid (also called fountain solution) and ink are applied to the plate surface that contains the hydrophilic and oleophilic areas. The hydrophilic areas are soaked with water in the dampening liquid and are thereby rendered oleophobic.

Various heat-mode plate materials are known which can be used as a lithographic master for printing with greasy inks. Ablative plates are the best known examples of so-called processless plates, i.e. plates which do not require any processing and therefore can be used as a printing plate immediately after exposure. The heat, which is generated in the recording layer of such ablative plates by light absorption of a laser beam, removes a hydrophilic or oleophilic topcoat to expose an underlying oleophilic respectively hydrophilic surface, thereby obtaining the necessary differentiation of ink-accepting and non-printing areas.

For example DE-A-2 448 325 discloses a [illegible] printing plate comprising on a [illegible] with a hydrophilic surface a layer [illegible] which can be [illegible] by [illegible] the plate.

obtained which can be used on an printing press without further processing. The plate is called a "direct negative" plate because it is suitable for direct exposure by a laser beam, no exposure of the plate through a film mask required, and because the areas of the recording material that have been exposed to the laser are rendered ink-accepting and define the image areas, i.e. the printing areas.

Other disclosures in **DE-A-2 448 325** concern "direct negative" printing plates comprising e.g. hydrophilic aluminum support coated with a water soluble laser light (Argon-488nm) absorbing dye or with a coating based on a mixture of hydrophilic polymer and laser light absorbing dye (Argon-488nm). Further examples of heat-mode recording materials for preparing "direct negative" printing plates have been described in e.g. **DE-A-2 607 207, DD-A-213 530, DD-A-217 645** and **DD-A-217 914**. These documents disclose heat-mode recording materials that contain an anodized aluminum support and a hydrophilic recording layer provided thereon. Laser exposure renders the exposed areas insoluble and ink-receptive, whereas the non-exposed areas remain hydrophilic and water-soluble. Such plates can also be used directly in the press without processing, because the non-exposed areas are removed by the dampening liquid during printing, thereby revealing the anodized aluminum support.

DD-A-155 407 discloses a processless heat-mode "direct negative" printing plate where a hydrophilic aluminum oxide layer is rendered oleophilic by direct laser heat-mode imaging.

The above heat-mode "direct negative" lithographic printing plates are characterized by a low recording speed and/or the obtained plates are of poor quality and durability.

EP-A-580 393 discloses an ablative lithographic printing plate directly imageable by laser discharge, the plate comprising a topmost first layer and a second layer underlying the first layer wherein the first layer is characterized by efficient absorption of infrared radiation and the first and second layer exhibit different affinities for at least one printing liquid.

EP-A-683 728 discloses a heat mode recording material comprising on a support having an ink receptive surface or being coated with an ink receptive layer a substance capable of converting light into heat and a hydrophilic surface layer having a thickness of not more than [illegible].

US 4,034,183 describes a [illegible] plate that comprises a [illegible] hydrophilic [illegible] on a support which is oxidized [illegible] to form an ink repelling or an ink [illegible] Both the examples and teachings require a high power laser and the run lengths of the resulting lithographic plates are limited.

US 3,832,948 describes both a printing plate with a hydrophilic layer that may be ablated by strong light from a hydrophobic support and also a printing plate with a hydrophobic layer that may be ablated from a hydrophilic support. However, no examples are given.

US 3,964,389 describes a processless printing plate based on the principle of laser transfer of material. This process is very sensitive to transfer defects and requires an additional donor sheet.

US 4,054,094 describes a process for making a lithographic printing plate by using a laser beam to etch away a thin top coating of polysilicic acid on a polyester base, thereby rendering the exposed areas receptive to ink. No details of run length or print quality are given, but it is expected that an non-crosslinked polymer such as polysilicic acid will wear off rapidly and give a short run length.

US 4,081,572 describes a method for preparing a printing master on a substrate by coating the substrate with a hydrophilic polyamic acid and then image-wise converting the polyamic acid to melanophilic polyimide with heat from a laser. No details of run length, image quality or ink water balance are given.

Japanese Kokai No. 55/105560 describes a method for preparation of a lithographic printing plate by laser [illegible] of a hydrophilic layer coated on a melanophilic support in which the hydrophilic layer contains colloidal silica and aluminum and xylan and a salt of a polyacrylic acid. No examples are given that disclose the use of a polyacrylic acid salt with a polyhydroxy polymer. No details on run length.

WO 92/09934 [illegible]

[illegible] tetramethyl pyrroyl [illegible]

[illegible]

All the examples illustrated in the present application employ a processless direct imageable printing plate which has a high sensitivity, good staining behavior and offers a high run length.

The published **EP-A no. 99202109, filed on 29.06.99,** discloses a negative-working heat-sensitive material for making lithographic plates comprising on the [illegible] a lithographic base having a hydrophilic surface, an [illegible] layer and a top [illegible] hydrophilic upper layer. The heat generated during exposure in the imaging layer removes the hydrophilic upper layer by ablation. However, the water-acceptance in the non-exposed areas is insufficient and, as a result, the plate has an inferior start-up behavior, i.e. the non-exposed areas in a certain amount of ink (a defect known as "toning") while printing the first 10 to 50 copies, which are lost due to bad print quality.

SUMMARY OF THE INVENTION

It is an [illegible] the present invention to provide a processless material that is suitable for [illegible] plate-making and is characterized by a high [illegible] quality, especially with regard to start-up behavior. This object is achieved by the material as claimed in [illegible] Preferred embodiments thereof are defined in the dependent claims.

PREFERRED EMBODIMENTS OF THE INVENTION

The lithographic printing plate of the present invention is [illegible] which comprises a lithographic base having a hydrophilic surface and a [illegible] layer and a top hydrophilic layer.

[illegible]

[illegible] least 61% by weight and more preferably at least 81% by weight.

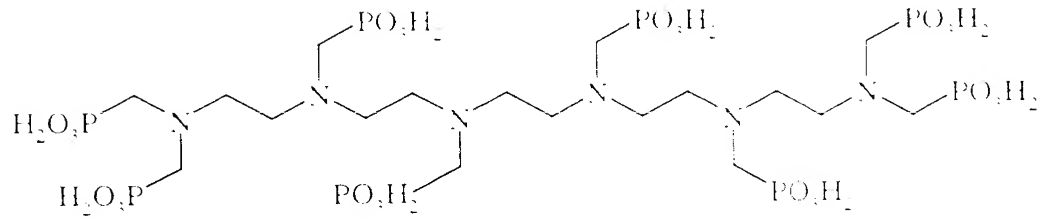
Hydrophilic layers [illegible] polyvinylacetate hydrolysed to an extent of at least 71% by weight hardened with a tetraalkyl orthosilicate, e.g. tetraethyl orthosilicate or tetramethyl orthosilicate as described in e.g. **US 3,476,937**, are particularly preferred because their use in the present heat-mode recording material results in excellent lithographic printing properties.

A further suitable [illegible] **EP-A- 514 990**. [illegible] comprises the hardening reaction [illegible] containing amine or amide functions having at least two free hydrogen e.g. amino modified dextrans and alkyds.

[illegible] porosity of the layer e.g. metal oxide particles which have particles of titanium [illegible] hydrophilic layer a uniform rough texture [illegible] hills and valleys. These particles are preferably oxides or [illegible]

imines etc. Besides traditional homopolymers or copolymers also branched matrix bodies like hyperbranched polymers or dendrimers could be applied.

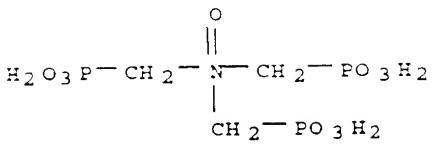
In particular multifunctional phosphonates known under the trade name Briquest are highly preferred. One of the suitable examples is Briquest 8106-25S = [[1,6,9,12-tetrakis(phosphonomethyl)-1,6,9,12-tetraaza tetradecane-1,14-diyl]-bis[nitrilobis(methylene)]]tetrakis-Phosphonic acid sodium salt:



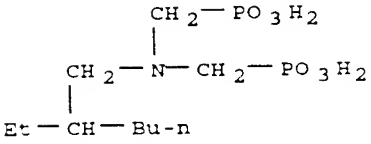
x Na

wherein x is an integer between zero and the total number of acid protons in the molecule. Other suitable Briquest grades are: Briquest 3010-25K ([(oxidonitrilo)tris(methylene)]tris-Phosphonic acid, potassium salt), Briquest [illegible] ([[(2-ethylhexyl)imino]bis(methylene)]bis-Phosphonic acid sodium salt, Briquest [illegible] ([1,2-ethanediylbis[nitrilobis(methylene)]]-tetrakis-Phosphonic acidtetraammonium salt), Briquest 785 ([[(phosphonomethyl)imino]bis[2,1-ethanediyl[(phosphonomethyl)imino]-2,1-ethanediylnitrilo]]bis(methylene)]]-Phosphonic acid tetrakis-sodium salt), Briquest ADPA-60AW (1-hydroxyethylidene-bis-Phosphonic acid, potassium salt), Briquest [illegible] ([[bis(phosphonomethyl)amino]ethyl]amino]methyl]-Phosphonic acid sodium salt), Briquest [illegible] ([[(2-ethylhexyl)imino]bis(methylene)]-Phosphonic acid, sodium salt), Briquest [illegible] ([nitrilotris(methylene)]tris-Phosphonic acid sodium salt), Briquest [illegible] A ([nitrilotris(methylene)]tris-Phosphonic acid), Briquest ADPA-60A (1-hydroxyethylidene-bis-Phosphonic acid) [illegible]

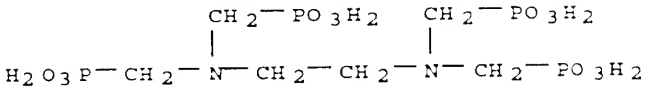
[illegible]



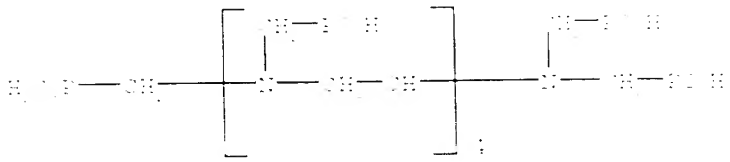
· x K

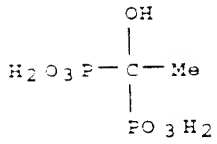


· x Na

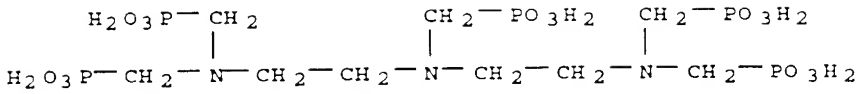


· 4 NH_3



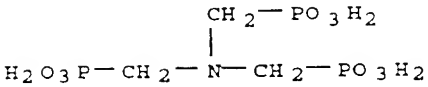


Briquest 301 :

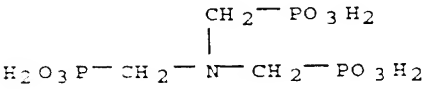


· x Na

Briquest 101-5IA :

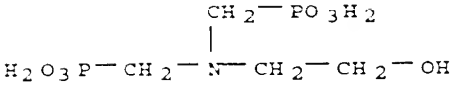


Briquest 11[illegible] AM :



· x Na

Briquest 5[illegible] :



· x Na

[illegible] EP-A- 601 240, GB-P- 1 419 512, FR-P- 2 300 354, US-P- 3 971 660, and US-P- 4 284 705.

[illegible]

[illegible] the wavelength range of the light source used [illegible] EP-A- 908 307 [illegible] metal oxides, silicates, carbides, nitrides and mixtures [illegible] GB-P-1 316 398 and DE-A- 2 512 038; [illegible]

GB-A- 1 084 070 DE-A- 4 423 140 DE-A- 4 417 907 EP-A- 659 909 EP-A- 537 633 DE-A- 4 001 466 EP-A- 292 801 EP-A- 291 760 US-P- 4 458 005.

which is provided with a hydrophilic layer. [illegible] layer. The silicone rubber is [illegible] silicone. The hydrophilic layer is preferably a hydrophilic layer obtained from a hydrophilic binder which is cross-linked with a hardening agent such as formaldehyde, glyoxal, a lysine nitrate or a hydrolyzed tetra-alkyl-orthosilicate. The latter is particularly preferred.

The hydrophilic binder for use in the present layers is e.g. a hydrophilic (co)polymer such as homopolymer and copolymers of vinyl alcohol, acrylamide, methylol acrylamide, methyl [illegible] acrylamide, acrylic acid, methacrylic acid, hydroxyethyl acrylate, hydroxyethyl methacrylate or maleic anhydride/vinylmethylether copolymers. The hydrophilicity of the (co)polymer or (co)polymer mixture used is preferably the same as or higher than the hydrophilicity of polyvinyl acetate hydrolysed to at least an extent of 60% by weight, preferably 70 % by weight.

The amount of hardening agent, in particular tetraalkyl orthosilicate, is preferably at least 0.2 parts per part by weight of hydrophilic binder, more preferably between 0.3 and 5 parts by weight, most preferably between 1 parts and 3 parts by weight.

The hydrophilic base layer may also contain other substances that increase the mechanical strength and porosity of the layer. For this purpose colloidal silica may be used. The colloidal silica employed may be in the form of any commercially available water dispersion of colloidal silica for example having an average particle size up to 40 nm, i.e. with a surface area sufficiently large to be capable of combination with the hydrophilic binder. Combinations of colloidal silica having different average particle sizes are also possible. The weight ratio colloidal silica [illegible] is preferably [illegible] and [illegible] is [illegible] parts by weight of [illegible] and [illegible] parts by weight of [illegible].

In addition to the hydrophilic binder and colloidal silica, the [illegible] may also contain [illegible] particles with an average [illegible] of between [illegible] and [illegible] nm which are particles of titanium dioxide or other heavy metal oxides. By incorporating these particles into the [illegible] hydrophilic base layer the [illegible] is increased and [illegible] of the [illegible] is obtained. [illegible] the [illegible] is preferably [illegible] and [illegible] parts by weight of [illegible] and [illegible] parts by weight of [illegible].

In addition to the hydrophilic [illegible] may also contain [illegible]

Particular examples of suitable hydrophilic [illegible] for use in accordance with the present invention are described in **EP-A- 601 240** **GB-P- 1 419 512** **FR-P- 2 300 354** **US-P- 3 971 660** and **US-P- 4 284 705**.

As flexible support it is both possible to use, in accordance with the present embodiment it is particularly preferred to use a plastic film e.g. polyethylene terephthalate film, cellulose acetate film, polystyrene film, polyvinyl chloride film, cellulose acetate film, polycarbonate film, etc. The plastic film support may be opaque or transparent.

It is particularly preferred to use a subbed support, with an adhesion improving layer, also called subbing layer, also used provided. Particularly suitable adhesion improving layers for use in accordance with the present invention comprise a hydrophilic binder and colloidal silica as disclosed in **EP-A- 619 524** **EP-A- 620 502** and **EP-A- 619 525**. Preferably, the amount of silica in the adhesion improving layer is between 200 mg per m^2 and 750 mg per m^2. Further, the ratio of silica to hydrophilic binder is preferably more than 1 and the surface area of the colloidal silica is preferably at least 300 m^2 per gram, more preferably at least 500 m^2 per gram.

Optionally the hydrophilic imaging material can be coated with an additional hydrophilic layer provided on top of the hydrophilic upper layer discussed above, which comprises an organic compound containing cationic groups as described in **EP-A no. 99202110, filed on 29.06.99.**

In accordance with the present invention the imaging material is image-wise exposed [illegible] the hydrophilic upper layer and where [illegible] hydrophilic. This is mostly the case when using short pixel dwell [illegible] dwell times are used, the hydrophilic layer may not [illegible] hydrophilic layer [illegible] with [illegible]

[illegible] part. A preferred [illegible] of [illegible] normally not regarded as a processing step, [illegible] treatment which provides the hydrophilic areas [illegible] other [illegible] which may affect the water-receptivity of these areas. By a gumming the remaining silanol [illegible] removed thereby avoiding [illegible] of the plate. At the same time the hydrophilic areas are covered with a thin layer of the gumming solution inducing a better starting print emulsion.

Imagewise exposure [illegible] is preferably an image-wise scanning exposure involving the use of a laser or L.E.D. Preferably lasers are used that operate in the infrared or near-infrared, i.e. wavelength range of 700-1500 nm. Most preferred are lasers [illegible] emitting in the near-infrared with an intensity higher than .1 mW/cm^2.

According to the present invention the plate is then ready for printing without an additional development and can be mounted on the printing press.

After [illegible] a further part of the imaging material is first [illegible] in the printing cylinder of the printing press and then imagewise exposed [illegible] by means of an on-press mounted image recording device. Subsequent to exposure the imaging material is ready for printing.

The printing plate of the present invention can also be used in the printing process as a removable sleeve printing plate. In this system the printing plate may be a liquid or a cylindrical [illegible] by means of a laser. Such cylindrical printing plate which has a [illegible] the diameter of the print cylinder can be fitted on the print cylinder instead of a mounted flat printing plate. More details about [illegible] are given in Research Disclosure, [illegible].

[illegible]

EXAMPLES

Preparation of the lithographic base

A 0.30 mm thick aluminum foil was degreased by immersing the foil in an aqueous solution containing 5 g/l of sodium hydroxide at 60°C and rinsed with demineralized water. The foil was then electrochemically grained using an alternating current in an aqueous solution containing 4 g/l of hydrochloric acid and 5 g/l of aluminum ions at a temperature of 35°C and a current density of 1200 A/m² to form a surface topography with an average center-line roughness Ra of 0.5 µm.

After rinsing with demineralized water the aluminum foil was etched with an aqueous solution containing 145 g/l of sulfuric acid at 60°C for 180 seconds and rinsed with demineralized water at 25°C for 30 seconds.

The foil was subsequently subjected to anodic oxidation in an aqueous solution containing 200 g/l of sulfuric acid at a temperature of 45°C, a voltage of 10 V and a current density of 150 A/m² for 120 seconds to form an anodic oxide layer of 3.0 g/m² of Al_2O_3, then washed with demineralized water, post-treated with a solution containing polyvinylphosphonic acid and a solution containing aluminum trichloride, and subsequently rinsed with demineralized water at 25°C and dried at 50°C for 5 minutes.

Preparation of the photosensitive layer

The coating layer was applied to the lithographic base at a wet coating thickness of 20 µm from a solution having the following composition:

[illegible]

- 1.44 g Vinyl modified PVA, trade mark [illegible]
- 10.72 g Ethylacetate

1.1 g Dimethyl formamide solution of the following composition :

- 1.15 g Dye 3 trade mark dye Solvent Red [illegible]
- 0.44 g Isopropanol

0.12 g Dymel solution of the following composition :

- 1.42 g Dymel 31 trade mark of E.I. Dupont
- 1.71 g Ethylacetate

1.76 g p-toluene sulfinic acid solution of the following composition :

- 5 mg Silica
- 0.176 g p-toluene sulfinic acid
- 1.584 g Ethylacetate

281.69 g Ethylacetate

211.41 g Ethylacetate

Preparation of the silica-linked hydrophilic upper layer

After drying the imaging layer, the hydrophilic layer was coated in a wet coating thickness of 21 um from a solution having the following composition :

7.1 g 7.1% Si[illegible] dispersion (Bindzil 30/360 from Eka Nobel, established with [illegible] MX 417 g hydroxyl ethyl cellulose, the dispersion contained 30 g polyvinyl alcohol versus 70 g average particle size 21 nm

7.1 g 7.1% hydrolysed tetramethyl orthosilicate (TMOS) in water ethanol 50:50.

1.1 g 1% wetting agent in water.

The pH of this solution was adjusted to 4 using [illegible]. After drying, the layer was hardened for 10 hours at 57°C [illegible].

Exposure and Processing

[illegible]

added to the coating solution of the hydrophilic surface layer. The details are given in table 1.

The resulting imaging materials were imaged on a Creo Trendsetter 3244T ™ at 2400 dpi operating at a drum speed of [illegible] rpm and a laser output of [illegible] Watt. After imaging the plate was mounted on a Heidelberg GTO52 press with a Dahlgren dampening system using K+E 800 Skinnex as ink and Rotamatic as dampening liquid. A compressible blanket was used. Subsequently the press was started by allowing the print cylinder with the imaging material mounted thereon to rotate. The dampener rollers of the press were first dropped on the imaging material so as to supply dampening liquid to the imaging material and after 10 revolutions of the print cylinder, the ink rollers were dropped to supply ink. After 10 further revolutions, the paper supply was started.

The start-up behaviour is defined as the number of sheets required before toning-free prints were obtained. The results are summarized in table 1.

Examples 4-7

The materials 4, 5, 6 and 7 were prepared in an identical way as the reference material with the proviso that in the coating solution of the hydrophilic layer a part of the polyvinylalcohol was replaced by a polymer which contains a sulfonic acid pendant group resulting in a layer composition as shown in table 1. The exposure, printing and evaluation method was the same as used in the reference examples 1-3.

Examples 8 and 9

The materials 8 and 9 were prepared in an identical way as the reference material with the proviso that a polymer which contains a sulfonic acid pendant group [illegible] added to the coating solution of the hydrophilic layer [illegible] as shown in table 1. The exposure, printing and evaluation method [illegible] the same as used in the reference examples [illegible].

[illegible] [illegible] [illegible] [illegible] Examples 1, 2 and 3

Example	Composition hydrophilic layer				Start up
	Alu	TMOS	polyvinylalcohol	extra binder	
1	71.0 %	22.0 %	7.0 %		100 prints
2	71.5 %	23.0 %	7.0 %	3.5 % PSVA *	5 prints
3	71.5 %	23.0 %	7.0 %	3.5 % PVPA	10 prints
4	73.5 %	29.0 %	7.0 %	3.5 % Briquest 8106 25S	10 prints

polyvinylsulfonic acid; Mn = 100000 g/mol; Mw = 200000 g/mol
polyvinylphosphonic acid; Mn = 6600 g/mol; Mw = 30000 g/mol
commercially available from Albright & Wilson

[illegible] [illegible] [illegible] [illegible] Examples 4, 5, 6 and 7

Example	Composition hydrophilic layer				Start up
	Alu	TEOS	polyvinylalcohol	PSVA (footnote * of Table 1)	
4	71.5 %	23.0 %	7.0 %	3.5 %	100 prints
5	71.5 %	23.0 %	5.0 %	3.5 %	10 prints
6	71.5 %	23.0 %	3.5 %	3.5 %	5 prints
7	71.5 %	23.0 %	2.0 %	5.0 %	5 prints
8	71.5 %	23.0 %	0.0 %	7.0 %	5 prints

Table [illegible] Start up behaviour of Examples 4 and 5

Example	Ingredients of ink receptive layer				Start up
	Silica	MMCC	polyvinylalcohol	extra binder	
[illegible]	[illegible]	[illegible]	7.5 %	[illegible]	20 prints
[illegible]	[illegible]	[illegible]	7.5 %	7.5 % Versa TL[illegible]	5 prints
5	76.5 %	26.5 %	6.5 %	6.5 % PSSA	1 prints

* PSSA = sodium salt of PSSA; ** commercially available from National Starch & Chem. Corp.; *** Versa TL[illegible].